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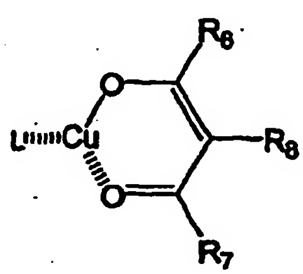
(54) $g(b)-DIKETONATOCOPPER(I) COMPLEX CONTAINING ALLENE COMPOUND AS LIGAND AND PROCESS FOR PRODUCING THE SAME

(57) A β-diketonatocopper(I) complex which contains as a ligand (L) an allene compound and is represented by formula (2)



(2)

wherein, R_6 and R_7 may be the same or different and each represents linear or branched C_{1-4} alkyl, C_{1-4} alkoxy, or linear or branched C_{1-4} fluoroalkyl, R_8 represents hydrogen or fluorine, and L represents the allene compound, and a process for producing the same. The complex is useful in forming a thin copper film by metal-organic vapor deposition (hereinafter abbreviated as MOCVD) method.

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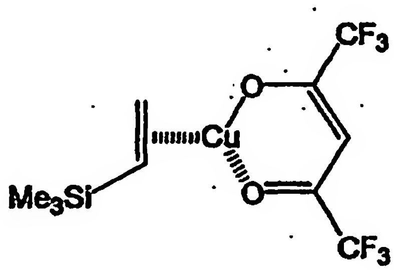
Description

Technical Field

[0001] The present invention relates to a β-diketonatocopper(I) complex useful in forming a thin copper film by metal-organic vapor deposition (hereinafter abbreviated as MOCVD) method and a process for producing the same.

Background Art

[0002] Conventionally, as a raw material for forming a thin copper film by MOCVD method, is well known β-diketonatocopper(I) complex comprising (vinyltrimethylsilane) (1,1,1,5,5,5-hexafluoro-2,4-pentanedionato) copper(I) of formula (a)



(α)

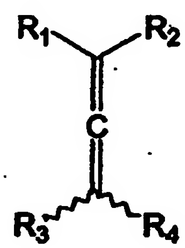
disclosed in Japanese Patent Laid-open No. Hei 5-59551.

[0003] However, vinyltrimethylsilane is used as a ligand for the β-diketonatocopper(I) complex of the formula (α). Conventionally, β-diketonatocopper(I) complex in which an allene compound is used as a ligand has not been known.

Disclosure of Invention

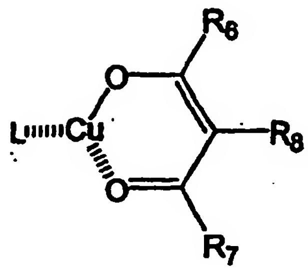
[0004] The present inventors research hard to find out novel β-diketonatocopper(I) complex in which an allene compound is used as a ligand from the above-mentioned viewpoint, and come to obtain β-diketonatocopper(I) complexes of formula (2) described below in which an allene compound of formula (1) described below is used as a ligand.

[0005] That is, the present invention relates to a β-diketonatocopper(I) complex which contains as a ligand (L) an allene compound of formula (1)



(1)

wherein R_1, R_2, R_3 and R_4 may be the same or different and each represents hydrogen, C_{1-4} alkyl or $(R_5)_3Si$-, or R_1 and R_2, together with the carbon atom bonding them, may form 3- to 6-member ring, or R_2 and R_3, together with the allene bond group bonding them, may form 8- to 10-member ring, R_5s may be the same or different and independently of one another represent linear or branched C_{1-4} alkyl,
and which is represented by formula (2)



(2)

wherein, R_6 and R_7 may be the same or different and each represents linear or branched C_{1-4} alkyl, C_{1-4} alkoxy, or linear or branched C_{1-4} fluoroalkyl, R_8 represents hydrogen or fluorine, and L represents the allene compound of formula (1).

[0006] Then, the present invention will be concretely explained.

[0007] The following is exemplified for each of the substituents in the chemical structural formula of allene compounds represented by formula (1) that is the ligand in the β-diketonatocopper(I) complexes of formula (2).

[0008] The substituents R_1, R_2, R_3 and R_4 include, for example H, Me, Et, n-Pr, n-Bu, i-Pr, i-Bu, s-Bu, t-Bu, Me_3Si, Et_3Si, n-Pr_3Si, n-Bu_3Si, i-Pr_3Si, i- Bu_3Si, s- Bu_3Si, t- Bu_3Si, Me_2(Et)Si, Me_2(n-Pr)Si, Me_2(n-Bu)Si, Me_2(i-Pr)Si, Me_2(i-Bu)Si, Me_2(s-Bu)Si, Me_2(t-Bu)Si, Et_2(Me)Si, Et_2(n-Pr)Si, Et_2(n-Bu)Si, Et_2(i-Pr)Si, Et_2(i-Bu)Si, Et_2(s-Bu)Si, Et_2(t-Bu)Si, n-Pr_2(Me)Si, n-Pr_2(Et)Si, n-Pr_2(i-Pr)Si, n-Pr_2(n-Bu)Si, n-Pr_2(s-Bu)Si, n-Pr_2(t-Bu)Si, n-Bu_2(Me)Si, n-Bu_2(Et)Si, n-Bu_2 (n-Pr)Si, n-Bu_2(i-Pr)Si, n-Bu_2(i-Bu)Si, n-Bu_2(s-Bu)Si, n-Bu_2(t-Bu)Si, i-Pr_2(Me)Si, i-Pr_2(Et)Si, i-Pr_2(n-Pr)Si, i-Pr_2(n-Bu) Si, i-Pr_2(s-Bu)Si, i-Pr_2(t-Bu)Si, i-Bu_2(Me)Si, i-Bu_2(Et)Si, i-Bu_2(n-Pr)Si, i-Bu_2(n-Bu)Si, i-Bu_2(i-Pr)Si, i-Bu_2(s-Bu)Si, i-Bu_2 (t-Bu)Si, s-Bu_2(Me)Si, s-Bu_2(Et)Si, s-Bu_2(n-Pr)Si, s-Bu_2(n-Bu)Si, s-Bu_2(i-Pr)Si, s-Bu_2(i-Bu)Si, s-Bu_2(t-Bu)Si, t-Bu_2(Me) Si, t-Bu_2(Et)Si, t-Bu_2(n-Pr)Si, t-Bu_2(n-Bu)Si, t-Bu_2(i-Pr)Si, t-Bu_2(i-Bu)Si or t-Bu_2(s-Bu)Si.

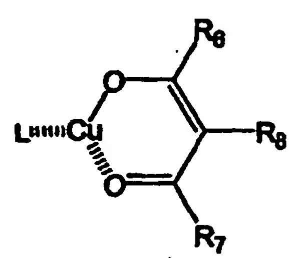
[0009] When R_1 and R_2, together with the carbon atom bonding them, form 3- to 6-member ring, the ring includes cyclopropane ring, cyclobutane ring, cyclopentane ring or cyclohexane ring.

[0010] When R_2 and R_3, together with the allene bond group bonding them, form 8- to 10-member ring, the ring includes cyclooctane ring, cyclononane ring or cyclodecane ring.

[0011] The following is exemplified for each of the substituents in the chemical structural formula of the β-diketonatocopper(I) complexes of formula (2).

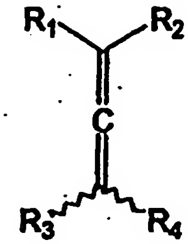
[0012] The substituents R_6 and R_7 include, for example, CF_3, C_2F_5, n-C_3F_7, i-C_3F_7, n-C_4F_9, Me, Et, n-Pr, n-Bu, i-Pr, i-Bu, s-Bu, t-Bu, MeO, EtO, n-PrO, n-BuO, i-PrO, i-BuO, s-BuO or t-BuO. In addition, the substituent R_8 includes, for example H or F.

[0013] The present invention also relates to a process for producing a β-diketonatocopper(I) complex represented by formula (2)



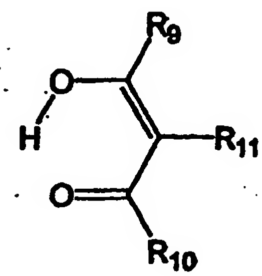
(2)

wherein, R_6 and R_7 may be the same or different and each represents linear or branched C_{1-4} alkyl, C_{1-4} alkoxy, or linear or branched C_{1-4} fluoroalkyl, R_8 represents hydrogen or fluorine, and L represents the allene compound of formula (1), characterized in that the process comprises reacting an allene compound of formula (1)



(1)

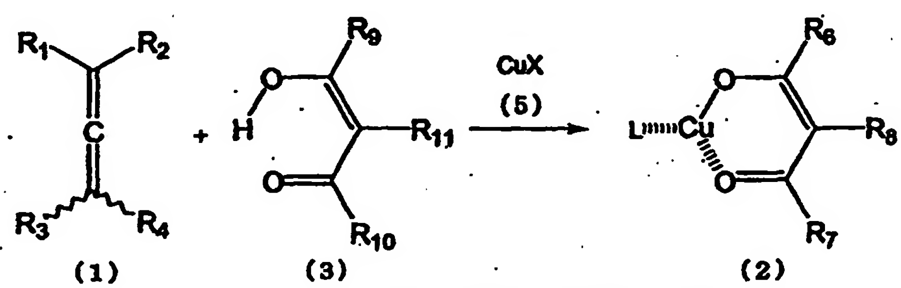
wherein R_1, R_2, R_3 and R_4 may be the same or different and each represents hydrogen, C_{1-4} alkyl or $(R_5)_3Si$-, or R_1 and R_2, together with the carbon atom bonding them, may form 3- to 6-member ring, or R_2 and R_3, together with the allene bond group bonding them, may form 8- to 10-member ring, R_5s may be the same or different and independently of one another represent linear or branched C_{1-4} alkyl, with an enol compound of formula (3)



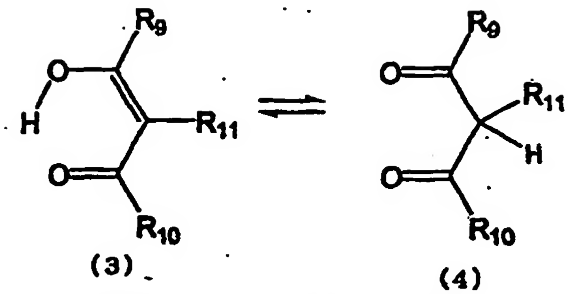
(3)

wherein R_9 and R_{10} may be the same or different and each represents linear or branched C_{1-4} alkyl, C_{1-4} alkoxy, or linear or branched C_{1-4} fluoroalkyl, R_{11} represents hydrogen or fluorine in the presence of a copper(I) compound.

[0014] Next, the process for producing a β-diketonatocopper(I) complex according to the present invention will be explained in more detail on the basis of reaction formulae (A) and (B).



REACTION FORMULA (A)



REACTION FORMULA (B)

in formula (1) in reaction formula (A), R_1, R_2, R_3 and R_4 may be the same or different and each represents hydrogen, C_{1-4} alkyl or $(R_5)_3Si$-, or R_1 and R_2, together with the carbon atom bonding them, may form 3- to 6-member ring, or R_2 and R_3, together with the allene bond group bonding them, may form 8- to 10-member ring, R_5s may be the same or different and independently of one another represent linear or branched C_{1-4} alkyl,
in formula (3) or (4), R_9 and R_{10} may be the same or different and each represents linear or branched C_{1-4} alkyl, C_{1-4} alkoxy, or linear or branched C_{1-4} fluoroalkyl, R_{11} represents hydrogen or fluorine,
in formula (2), R_6 and R_7 may be the same or different and each represents linear or branched C_{1-4} alkyl, C_{1-4} alkoxy, or linear or branched C_{1-4} fluoroalkyl, R_8 represents hydrogen or fluorine, and L represents the allene compound of formula (1).

[0015] In the reaction represented by reaction formula (A), a β-diketonatocopper(I) complex in which an allene compound is coordinated can be synthesized by reacting an allene compound of formula (1) with an enol compound of formula (3) or a carbonyl compound of formula (4) (the compound of formula (4) is a tautomer of the compound of formula (3)) together with a copper(I) compound (CuX) of formula (5) optionally in the presence of a base (for example, inorganic base, such as sodium hydride, potassium hydride, sodium amide, potassium tertiary butoxide, potassium carbonate or the like).

[0016] The copper(I) compound includes, for example, Cu_2O, CuF, CuCl, CuBr, CuI, CuOAc, CuCN, CuSCN, CuOTf and so on.

[0017] The enol compound of formula (3) is a tautomer of the carbonyl compound of formula (4) as indicated in reaction formula (B).

[0018] The molar ratio of the allene compound to the enol compound may be arbitrarily set. However, it is preferable that the enol compound and allene compound are mixed in an amount equimolar or close thereto. For example, the molar ratio of the enol compound to the allene compound may be 0.5 to 1.5.

[0019] The molar ratio of the allene compound to the copper(I) compound may be arbitrarily set. However, it is preferable that copper atoms in the copper(I) compound are equimolar with allene compound or that an excessive of the copper atoms is mixed with the allene compound. For example, the molar ratio of the copper atoms to the allene compound may be 0.5 to 3. The molar ratio of the base to the allene compound may be arbitrarily set. However, it is preferable that the base is equimolar with the allene compound or that an excessive of the base is mixed with the allene compound. For example, the molar ratio of the base to the allene compound may be 0.5 to 3.

[0020] Although the reaction temperature is not particularly limited, the reaction may be carried out generally at a temperature between -110°C and a boiling point of the solvent used in the reaction.

[0021] It is preferable to use solvents that do not participate in the reaction. The solvents that can be used include hydrocarbons (such as, hexane, pentane, benzene, toluene or the like), ethers (such as, diethyl ether, monoglyme, isopropyl ether, tetrahydrofuran, 1,4-dioxane or the like) and halogenated hydrocarbons (such as, dichloromethane, chloroform, dichloroethane or the like).

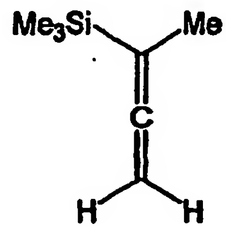
[0022] The β-diketonatocopper(I) complex according to the present invention is useful as a compound for forming a thin copper film by MOCVD method.

Best Mode for carrying out the Invention

[0023] The present invention will be concretely described on the basis of the following examples, but the present invention is not limited thereto at all.

(Example 1)

[0024] Under nitrogen atmosphere, into 3.0 g of copper(I) oxide was poured 30 ml of dry dichloromethane that was fully degassed and the atmosphere of which was replaced with nitrogen to give a suspension solution. 1.77 g of 1-methyl-1-(trimethylsilyl) allene was added to the solution with vigorously stirring, then 3.2 g of 1,1,1,5,5,5-hexafluoro-2,4-pentanedione was slowly added from a dropping funnel. After the reaction solution was stirred for 12 hours, the solution was filtered under nitrogen atmosphere, and the filtrate was concentrated under reduced pressure at room temperature to give a green liquid. The liquid was purified through a column chromatography to give 4.2 g of [1-methyl-1-(trimethylsilyl) allene] (1,1,1,5,5,5-hexafluoro-2,4-pentanedionato) copper(I) containing 1-methyl-1-(trimethylsilyl) allene as a ligand represented by formula (6)



(6)

as an yellow liquid.

[0025] The resulting β-diketonatocopper(I) complex was identified with ^{1}H-NMR and ^{13}C-NMR. ^{1}H-NMR (δ, $CDCl_3$) 0.19 (s, 9H), 1.97-1.99 (m, 3H), 4.14-4.16 (m, 2H), 6.15 (s, 1H). ^{13}C-NMR (δ, $CDCl_3$) -2.29 (3C), 17.09, 51.00, 90.21, 96.13, 117.69 (q, $J_{C\text{-}F}$=283.7Hz, 2C), 173.87, 178.33 (q, $J_{C\text{-}C\text{-}F}$=34.5Hz, 2C).

[0026] For evaluating the vaporization characteristic of the resulting β-diketonatocopper(I) complex, the thermogravimetric curve (heating rate: 10°C/min., under nitrogen atmosphere) was measured. Consequently, it was found that the complex has extremely high volatility and good vaporization characteristic. Boiling point: 140-164°C.

(Example 2)

[0027] Under nitrogen atmosphere, into 3.0 g of copper(I) oxide was poured 30 ml of dry dichloromethane that was fully degassed and the atmosphere of which was replaced with nitrogen to give a suspension solution. 1.72 g of 1,2-cyclononadiene was added to the solution with vigorously stirring, then 3.23 g of 1,1,1,5,5,5-hexafluoro-2,4-pentanedione was slowly added from a dropping funnel. After the reaction solution was stirred for 4 hours, the solution was filtered under nitrogen atmosphere, and the filtrate was concentrated under reduced pressure at room temperature to give a green liquid.

[0028] The liquid was purified through a column chromatography to give 5.63 g of (1,2-cyclononadiene) (1,1,1,5,5,5-hexafluoro-2,4-pentanedionato) copper(I) containing 1,2-cyclononadiene as a ligand represented by formula (7)

(7)

as an yellow solid.

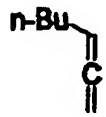
[0029] The resulting β-diketonatocopper(I) complex was identified with 1H-NMR and ^{13}C-NMR. ^{1}H-NMR (δ, $CDCl_3$) 1.38-1.77 (m, 8H), 2.06-2.24 (m, 4H), 5.26-5.32 (m, 2H), 6.10 (s, 1H).

^{13}C-NMR (δ, $CDCl_3$) 23.65, 25.49, 28.44, 88.28, 90.61, 118.65 (q, $J_{C\text{-}F}$=284.1Hz, 2C), 173.83, 178.63 (q, $J_{C\text{-}C\text{-}F}$=34.6Hz, 2C).

[0030] For evaluating the vaporization characteristic of the resulting β-diketonatocopper(I) complex, the thermogravimetric curve (heating rate: 10°C/min., under nitrogen atmosphere) was measured. Consequently, the complex had a melting point of 46.8°C and a boiling point of 195.6°C.

(Example 3)

[0031] In a similar manner as Example 2, starting from 3.0 g of copper(I) oxide, 1.30 g of 1,2-heptadiene and 3.23 g of 1,1,1,5,5,5-hexafluoro-2,4-pentanedione, 2.82 g of (1,2-heptadiene) (1,1,1,5,5,5-hexafluoro-2,4-pentanedionato) copper(I) containing 1,2-heptadiene as a ligand represented by formula (8)



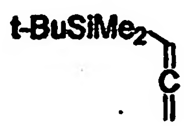
(8)

was obtained as an yellow liquid.
^{1}H-NMR (δ, $CDCl_3$) 0.89 (t, J=7.3Hz, 3H), 1.30-1.42 (m, 2H), 1.42-1.54 (m, 2H), 2.15-2.27 (m, 2H), 4.33-4.40 (m, 2H), 5.45-5.55 (m, 1H), 6.13 (s, 1H). ^{13}C-NMR (δ, $CDCl_3$) 13.95, 22.46, 31.50, 31.70, 55.72, 90.76, 92.44, 117.96 (q, $J_{C\text{-}F}$=283.7Hz, 2C), 165.80, 178.85 (q, $J_{C\text{-}C\text{-}F}$=34.5Hz, 2C).

[0032] For evaluating the vaporization characteristic of the resulting β-diketonatocopper(I) complex, the thermogravimetric curve (heating rate: 10°C/min., under nitrogen atmosphere) was measured. Consequently, the complex had a boiling point of 150.0°C.

(Example 4)

[0033] In a similar manner as Example 2, starting from 3.0 g of copper(I) oxide, 2.16 g of 1-(dimethyl-tert-butylsilyl) allene and 3.23 g of 1,1,1,5,5,5-hexafluoro-2,4-pentanedione, 3.47 g of [(1-(dimethyl-tert-butylsilyl) allene)] (1,1,1,5,5,5-hexafluoro-2,4-pentanedionato) copper(I) containing 1-(dimethyl-tert-butylsilyl) allene as a ligand represented by formula (9)



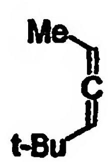
(9)

was obtained as an yellow liquid. ^{1}H-NMR (δ, $CDCl_3$) 0.20 (s, 6H), 0.97 (s, 9H), 4.35 (d, J=4.0Hz, 2H), 4.87 (t, J=4.4Hz, 1H), 6.15 (s, 1H). ^{13}C-NMR (δ, $CDCl_3$)-5.40, 18.72, 26.61, 55.36, 69.50, 90.93, 117.94 (q, $J_{C\text{-}F}$=283.8Hz, 2C), 159.51, 178.96 (q, $J_{C\text{-}C\text{-}F}$=34.8Hz, 2C).

[0034] For evaluating the vaporization characteristic of the resulting β-diketonatocopper(I) complex, the thermogravimetric curve (heating rate: 10°C/min., under nitrogen atmosphere) was measured. Consequently, the complex had a boiling point of 140.0°C.

(Example 5)

[0035] In a similar manner as Example 2, starting from 3.0 g of copper(I) oxide, 1.54 g of 1-(tert-butyl)-2-methyl allene and 3.23 g of 1,1,1,5,5,5-hexafluoro-2,4-pentanedione, 1.78 g of [1-(tert-butyl)-2-methyl allene] (1,1,1,5,5,5-hexafluoro-2,4-pentanedionato) copper(I) containing 1-(tert-butyl)-2-methyl allene as a ligand represented by formula (10)



(10)

was obtained as an yellow liquid. ^{1}H-NMR (δ, $CDCl_3$) 1.18 (s, 9H), 1.89-1.98 (m, 3H), 5.30-5.40 (m, 2H), 6.11 (s,

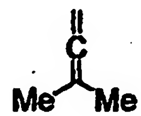
1H). ^{13}C-NMR (δ, $CDCl_3$) 18.42, 30.41, 36.41, 79.79, 90.77, 93.20, 117.94 (q, J_{C-F}=283.8Hz, 2C), 150.16, 178.78 (q, J_{C-C-F}=34.9Hz, 2C).

[0036] For evaluating the vaporization characteristic of the resulting p-diketonatocopper(I) complex, the thermogravimetric curve (heating rate: 10°C/min., under nitrogen atmosphere) was measured. Consequently, the complex had a boiling point of 147.0°C.

(Example 6)

[0037] Under nitrogen atmosphere, into 3.0 g of copper(I) oxide was poured 30 ml of dry dichloromethane that was fully degassed and the atmosphere of which was replaced with nitrogen to give a suspension solution. 0.96 g of 1,1-dimethyl allene was added to the solution with vigorously stirring, then 3.2 g of 1,1,1,5,5,5-hexafluoro-2,4-pentanedione was slowly added from a dropping funnel. After the reaction solution was stirred for 12 hours, the solution was filtered under nitrogen atmosphere, and the filtrate was concentrated under reduced pressure at room temperature to give a green liquid.

[0038] The liquid was purified through a column chromatography to give 2.3 g of (1,1-dimethyl allene) (1,1,1,5,5,5-hexafluoro-2,4-pentanedionato) copper(I) containing 1,1-dimethyl allene as a ligand represented by formula (11).



(11)

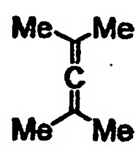
as an yellow liquid.

[0039] The resulting β-diketonatocopper(I) complex was identified with ^{1}H-NMR and ^{13}C-NMR. ^{1}H-NMR (δ, $CDCl_3$) 1.96 (t, J=2.8Hz, 6H), 4.16 (t, J=2.8Hz, 2H), 6.16 (s, 1H). ^{13}C-NMR (δ, $CDCl_3$) 22.63 (2C), 50.03, 90.24, 108.41, 117.75 (q, J_{C-F}=284.9Hz, 2C), 175.10, 178.40 (q, J_{C-C-F}=34.7Hz, 2C).

(Example 7)

[0040] Under nitrogen atmosphere, into 3.0 g of copper(I) oxide was poured 30 ml of dry dichloromethane that was fully degassed and the atmosphere of which was replaced with nitrogen to give a suspension solution. 1.35 g of 1,1,3,3-tetramethyl allene was added to the solution with vigorously stirring, then 3.2 g of 1,1,1,5,5,5-hexafluoro-2,4-pentanedione was slowly added from a dropping funnel. After the reaction solution was stirred for 12 hours, the solution was filtered under nitrogen atmosphere, and the filtrate was concentrated under reduced pressure at room temperature to give a green liquid.

[0041] The liquid was purified through a column chromatography to give 3.8 g of (1,1,3,3-tetramethyl allene) (1,1,1,5,5,5-hexafluoro-2,4-pentanedionato) copper(I) containing 1,1,3,3-tetramethyl allene as a ligand represented by formula (12)



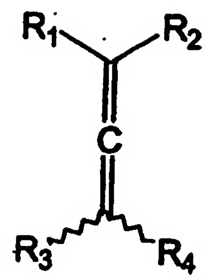
(12)

as an yellow solid.

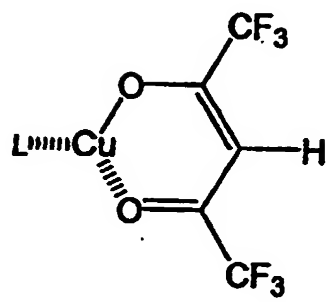
[0042] The resulting β-diketonatocopper(I) complex was identified with ^{1}H-NMR and ^{13}C-NMR. ^{1}H-NMR (δ, $CDCl_3$) 2.00 (s, 12H), 6.18 (s, 2H). ^{13}C-NMR (δ, $CDCl_3$) 24.84 (4C), 90.50 (2C), 93.25 (2C), 117.81 (q, J_{C-F}=285.3Hz, 4C), 145.33, 178.61 (q, J_{C-C-F}=34.7Hz, 4C).

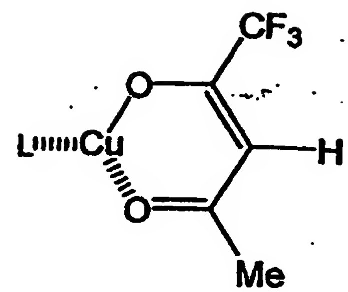
[0043] Table 1 indicates the β-diketonatocopper(I) complexes (including ones synthesized in Examples described above) of the present invention synthesized according to the producing process or Examples described above along with allene compounds of their ligands (L) [formula (1)], but the present invention is not limited thereto.

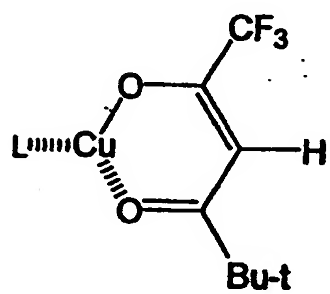
Table 1

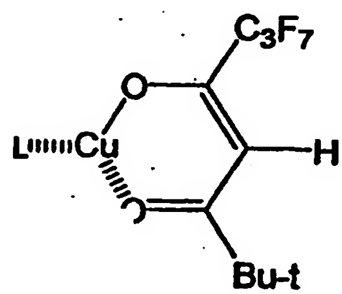


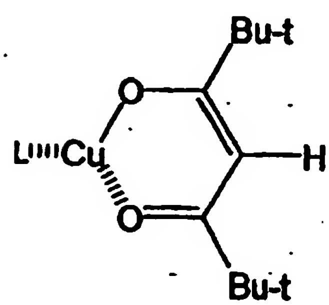
(1)











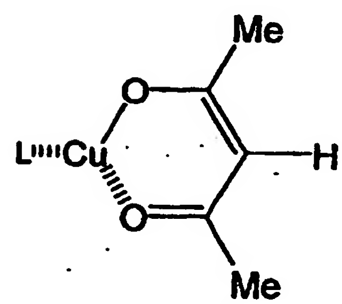
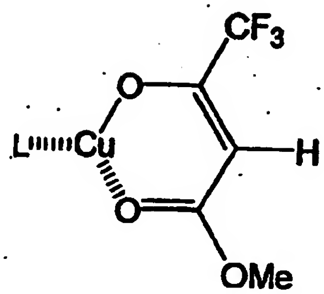


Table 1 (continued)



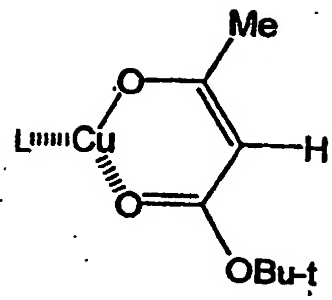


Table 1 (continued)

R_1	R_2	R_3	R_4
H	H	H	H
H	Me	H	H
H	Et	H	H
H	n-Pr	H	H
H	n-Bu	H	H
H	i-Pr	H	H
H	i-Bu	H	H
H	s-Bu	H	H
H	t-Bu	H	H
H	Me_3Si	H	H
H	Et_3Si	H	H
H	$n\text{-}Pr_3Si$	H	H
H	$n\text{-}Bu_3Si$	H	H
H	$i\text{-}Pr_3Si$	H	H
H	$Me_2(Et)Si$	H	H
H	$Me_2(n\text{-}Pr)Si$	H	H
H	$Me_2(i\text{-}Pr)Si$	H	H
H	$Me_2(t\text{-}Bu)Si$	H	H
Me	Me	H	H
Me	Et	H	H

Table 1 (continued)

R_1	R_2	R_3	R_4
Me	n-Pr	H	H
Me	n-Bu	H	H
Me	i-Pr	H	H
Me	i-Bu	H	H
Me	s-Bu	H	H
Me	t-Bu	H	H
Me	Me_3Si	H	H
Me	Et_3Si	H	H
Me	$n\text{-}Pr_3Si$	H	H
Me	$n\text{-}Bu_3Si$	H	H
Me	$i\text{-}Pr_3Si$	H	H
Me	$Me_2(Et)Si$	H	H
Me	$Me_2(n\text{-}Pr)Si$	H	H
Me	$Me_2(i\text{-}Pr)Si$	H	H
Me	$Me_2(t\text{-}Bu)Si$	H	H
Et	Et	H	H
Et	n-Pr	H	H
Et	n-Bu	H	H
Et	i-Pr	H	H
Et	i-Bu	H	H

Table 1 (continued)

R_1	R_2	R_3	R_4
Et	s-Bu	H	H
Et	t-Bu	H	H
n-Pr	n-Pr	H	H
n-Pr	n-Bu	H	H
n-Pr	i-Pr	H	H
n-Pr	i-Bu	H	H
n-Pr	s-Bu	H	H
n-Pr	t-Bu	H	H
n-Bu	n-Pr	H	H
n-Bu	i-Pr	H	H
n-Bu	i-Bu	H	H
n-Bu	s-Bu	H	H
n-Bu	t-Bu	H	H
Me_3Si	Et	H	H
Me_3Si	n-Pr	H	H
Me_3Si	n-Bu	H	H
Me_3Si	i-Pr	H	H
Me_3Si	i-Bu	H	H
Me_3Si	s-Bu	H	H
Me_3Si	t-Bu	H	H

Table 1 (continued)

R_1	R_2	R_3	R_4
n-Bu_3Si	Et	H	H
n-Bu_3Si	n-Pr	H	H
n-Bu_3Si	n-Bu	H	H
n-Bu_3Si	i-Pr	H	H
n-Bu_3Si	i-Bu	H	H
n-Bu_3Si	s-Bu	H	H
n-Bu_3Si	t-Bu	H	H
Me_2(t-Bu)Si	Et	H	H
Me_2(t-Bu)Si	n-Pr	H	H
Me_2(t-Bu)Si	n-Bu	H	H
Me_2(t-Bu)Si	i-Pr	H	H
Me_2(t-Bu)Si	i-Bu	H	H
Me_2(t-Bu)Si	s-Bu	H	H
Me_2(t-Bu)Si	t-Bu	H	H
Me_3Si	Me_3Si	H	H
Me_3Si	Me_2(t-Bu)Si	H	H
-$(CH_2)_2$-		H	H
-$(CH_2)_5$-		H	H

Table 1 (continued)

R_1	R_2	R_3	R_4
Me	H	Me	H
Me	H	Et	H
Me	H	n-Pr	H
Me	H	n-Bu	H
Me	H	i-Pr	H
Me	H	i-Bu	H
Me	H	s-Bu	H
Me	H	t-Bu	H
Me	H	Me_3Si	H
Me	H	Et_3Si	H
Me	H	n-Pr_3Si	H
Me	H	n-Bu_3Si	H
Me	H	i-Pr_3Si	H
Me	H	Me_2(Et)Si	H
Me	H	Me_2(n-Pr)Si	H
Me	H	Me_2(i-Pr)Si	H
Me	H	Me_2(t-Bu)Si	H
Et	H	Et	H
Et	H	n-Pr	H
Et	H	n-Bu	H

Table 1 (continued)

R_1	R_2	R_3	R_4
Et	H	i-Pr	H
Et	H	i-Bu	H
Et	H	s-Bu	H
Et	H	t-Bu	H
n-Pr	H	n-Pr	H
n-Pr	H	n-Bu	H
n-Pr	H	i-Pr	H
n-Pr	H	i-Bu	H
n-Pr	H	s-Bu	H
n-Pr	H	t-Bu	H
n-Bu	H	n-Pr	H
n-Bu	H	i-Pr	H
n-Bu	H	i-Bu	H
n-Bu	H	s-Bu	H
n-Bu	H	t-Bu	H
Me_3Si	H	Et	H
Me_3Si	H	n-Pr	H
Me_3Si	H	n-Bu	H
Me_3Si	H	i-Pr	H
Me_3Si	H	i-Bu	H

Table 1 (continued)

R_1	R_2	R_3	R_4
Me_3Si	H	s-Bu	H
Me_3Si	H	t-Bu	H
$n\text{-}Bu_3Si$	H	Et	H
$n\text{-}Bu_3Si$	H	n-Pr	H
$n\text{-}Bu_3Si$	H	n-Bu	H
$n\text{-}Bu_3Si$	H	i-Pr	H
$n\text{-}Bu_3Si$	H	i-Bu	H
$n\text{-}Bu_3Si$	H	s-Bu	H
$n\text{-}Bu_3Si$	H	t-Bu	H
$Me_2(t\text{-}Bu)Si$	H	Et	H
$Me_2(t\text{-}Bu)Si$	H	n-Pr	H
$Me_2(t\text{-}Bu)Si$	H	n-Bu	H
$Me_2(t\text{-}Bu)Si$	H	i-Pr	H
$Me_2(t\text{-}Bu)Si$	H	i-Bu	H
$Me_2(t\text{-}Bu)Si$	H	s-Bu	H
$Me_2(t\text{-}Bu)Si$	H	t-Bu	H
Me_3Si	H	Me_3Si	H
Me_3Si	H	$Me_2(t\text{-}Bu)Si$	H
H	$-(CH_2)_6-$		H
H	$-(CH_2)_7-$		H

Table 1 (continued)

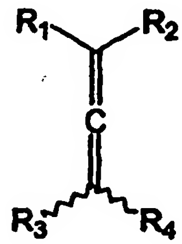
R_1	R_2	R_3	R_4
Me	Me	Me	H
Me	Et	Me	H
Me	Et	i-Bu	H
Me	i-Bu	Me	H
Me	Me	Me_3Si	H
Me	Me_3Si	n-Bu	H
n-Bu	Me_3Si	Me	H
Me	Me_3Si	Me_3Si	H
Me_3Si	Me_3Si	Me_3Si	H
$-(CH_2)_4-$		Me	H
$-(CH_2)_5-$		Me	H
Me	$-(CH_2)_6-$		H
Me	Me	Me	Me
Me	n-Bu	Me	Me
Me	Me_3Si	Me	n-Pr
n-Bu	Me_3Si	Me	Me
Me	Me_3Si	n-Bu	n-Bu
Me_3Si	Me_3Si	Me_3Si	Me_3Si
$-(CH_2)_5-$		Me	n-Pr

Industrial Applicability

[0044] The present invention provides novel β-diketonatocopper(I) complexes and processes for producing the same. The β-diketonatocopper(I) complexes according to the present invention are useful as compounds for forming a thin copper film by MOCVD method.

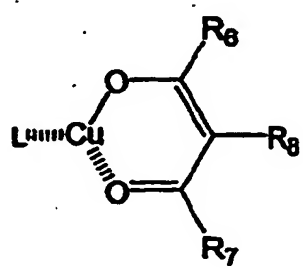
Claims

1. A β-diketonatocopper(I) complex which contains as a ligand (L) an allene compound of formula (1)



(1)

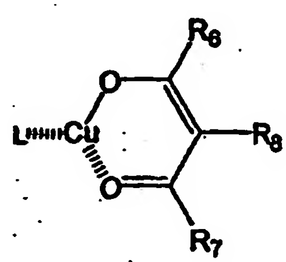
wherein R_1, R_2, R_3 and R_4 may be the same or different and each represents hydrogen, C_{1-4} alkyl or $(R_5)_3Si$-, or R_1 and R_2, together with the carbon atom bonding them, may form 3- to 6-member ring, or R_2 and R_3, together with the allene bond group bonding them, may form 8- to 10-member ring, R_5s may be the same or different and independently of one another represent linear or branched C_{1-4} alkyl,
and which is represented by formula (2)



(2)

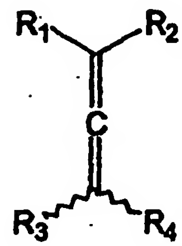
wherein, R_6 and R_7 may be the same or different and each represents linear or branched C_{1-4}, alkyl, C_{1-4} alkoxy, or linear or branched C_{1-4} fluoroalkyl, R_8 represents hydrogen or fluorine, and L represents the allene compound of formula (1).

2. A process for producing a β-diketonatocopper(I) complex represented by formula (2)



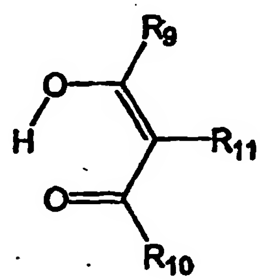
(2)

wherein, R_6 and R_7 may be the same or different and each represents linear or branched C_{1-4} alkyl, C_{1-4} alkoxy, or linear or branched C_{1-4} fluoroalkyl, R_8 represents hydrogen or fluorine, and L represents the allene compound of formula (1), **characterized in that** the process comprises reacting an allene compound of formula (1)



(1)

wherein R_1, R_2, R_3 and R_4 may be the same or different and each represents hydrogen, C_{1-4} alkyl or $(R_5)_3Si$-, or R_1 and R_2, together with the carbon atom bonding them, may form 3- to 6-member ring, or R_2 and R_3, together with the allene bond group bonding them, may form 8- to 10-member ring, R_5s may be the same or different and independently of one another represent linear or branched C_{1-4} alkyl, with an enol compound of formula (3)



(3)

wherein R_9 and R_{10} may be the same or different and each represents linear or branched C_{1-4} alkyl, C_{1-4} alkoxy, or linear or branched C_{1-4} fluoroalkyl, R_{11} represents hydrogen or fluorine in the presence of a copper(I) compound.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP01/01956

A. CLASSIFICATION OF SUBJECT MATTER
Int.Cl[7] C07C49/92, 45/77, 11/14, 13/02, C07F7/08
//C07F1/08, C23C16/18

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
Int.Cl[7] C07C49/92, 45/77, 11/14, 13/02, C07F7/08,
C07F1/08, C23C16/18

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP, 498269, A2 (AIR PRODUCTS AND CHEMICALS, INC.), 12 August, 1992 (12.08.92) & US, 5085731, A & JP, 5-59551, A & KR, 9411709, B1	1,2
A	EP, 533070, A2 (AIR PRODUCTS AND CHEMICALS, INC.), 24 March, 1993 (24.03.93) & US, 5187300, A & JP, 5-202476, A & KR, 9504895, B1	1,2
A	EP, 493754, A1 (AIR PRODUCTS AND CHEMICALS, INC.), 08 July, 1992 (08.07.92) & US, 5098516, A & JP, 4-318170, A & KR, 9405327, B1 & IE, 73257, B	1,2

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
04 April, 2001 (04.04.01)	17 April, 2001 (17.04.01)
Name and mailing address of the ISA/ Japanese Patent Office	Authorized officer
Facsimile No.	Telephone No.

Form PCT/ISA/210 (second sheet) (July 1992)